8-1997

Rapid Analysis of Wood Using Transient Infrared Spectroscopy and Photoacoustic Spectroscopy with PLS Regression

Stanley J. Bajic
Iowa State University, sjbajic@ameslab.gov

Roger W. Jones
Iowa State University, jonesrw@ameslab.gov

John F. McClelland
Iowa State University, mcclelland@ameslab.gov

Bonnie R. Hames
National Renewable Energy Laboratory

Robert R. Meglen
National Renewable Energy Laboratory

Rapid analysis of wood using transient infrared spectroscopy and photoacoustic spectroscopy with PLS regression

Stanley J. Bajic, Roger W. Jones, John F. McClelland, Bonnie R. Hames, and Robert R. Meglen

Citation: AIP Conference Proceedings **430**, 466 (1998); doi: 10.1063/1.55710
View online: http://dx.doi.org/10.1063/1.55710
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/430?ver=pdfcov
Published by the AIP Publishing

Rapid Analysis of Wood Using Transient Infrared Spectroscopy and Photoacoustic Spectroscopy with PLS Regression

Stanley J. Bajic[1], Roger W. Jones[1], John F. McClelland[1],
Bonnie R. Hames[2], and Robert R. Meglen[2]

[1]*Ames Laboratory, Iowa State University, Ames, IA 50011 U. S. A. and*
[2]*National Renewable Energy Laboratory, Golden, CO 80401 U. S. A.*

In the forest products industry, improved methods are needed for rapid analysis of wood and paper products. Currently, the best methods for determining chemical and physical properties of wood-based materials require considerable sample preparation and analysis time. Consequently, quantitative information is often not obtained on a time scale suitable for process monitoring, control, and quality assurance. The primary barriers to practical utilization of conventional infrared methods are the opaqueness and poor reflection properties of the wood-based materials. This paper demonstrates how photoacoustic and transient infrared spectroscopies have been combined with chemometric techniques to overcome the limitations of conventional infrared spectroscopies and to permit rapid chemical and physical characterization of wood chips. Both photoacoustic and transient infrared spectroscopic methods are examined as rapid at- and on-line techniques for feedstock identification and chemical composition analysis prior to processing.

INTRODUCTION

Methods for obtaining rapid, high quality and reproducible qualitative and quantitative data are needed in the paper and pulp industry to maintain process control. Currently, the best analytical methods for the determination of the chemical composition of wood require considerable sample size, elaborate sample preparation and several days of analysis time. Various chemical properties of wood can readily be determined from FTIR spectra of ground wood.(1-3) This paper demonstrates two methods, FTIR photoacoustic spectroscopy (FTIR-PAS) and transient infrared spectroscopy (TIRS), each combined with partial least squares (PLS) regression as faster and simpler alternatives for the characterization of feedstocks at and on line, respectively. Results demonstrating species identification (qualitative analysis) and chemical composition (quantitative analysis) for both analytical methods are presented.

FTIR-PAS can acquire both near infrared and mid-infrared spectra from small (submilliliter) samples of milled wood with sufficient precision for quantitative results when used with PLS regression. Transient infrared spectroscopy brings the capabilities of PAS to the process line. In TIRS, the surface of the moving material is heated with a jet of hot air. The warmed surface radiates in the mid-infrared region, and its emission spectrum is captured with an FTIR spectrometer. The heated surface is sufficiently thin that its emission is not overly affected by self-absorption, and it has the characteristic structure found in conventional spectra. Combining TIRS with PLS regression can provide real-time, on-line quantitative analysis of wood as well as other solid materials.(4)

EXPERIMENTAL

Eight different species of wood chips were acquired from several industrial collaborators and analyzed. Douglas fir, Southern yellow pines, acacia, eucalyptus, loblolly pine, ponderosa pine, white fir and a variety of mixed Southern hardwoods (yellow oak, hickory, blackgum and sweet gum) were harvested, chipped and milled for chemical analysis and spectroscopic characterization.

Photoacoustic wood data were measured from milled samples and collected on a Bio-Rad Digilab FTS-60A FT-IR spectrometer equipped with an MTEC model 200 photoacoustic cell. Two-hundred fifty six scans were co-added at 2.5 kHz (<5 mins) for each sample. All spectra were normalized to carbon black.

TIRS data were collected on a Bomem MB 100 FT-IR spectrometer equipped with an external focussing mirror and a wide-band MCT detector cooled with liquid nitrogen. The normal infrared source was replaced by a cold surface. A platter was positioned so that wood chips could be rotated within the spectrometer's field of view simulating a feedstock process line. A heated gas jet was also mounted to the

CP430, *Fourier Transform Spectroscopy:* 11th International Conference
edited by J.A. de Haseth

spectrometer so that it could be aimed onto the moving wood chips. Spectra were acquired while the chips were moving at 1.8 m/s (350 ft/min).

Calibration modeling was performed on all data sets using PLS. ASTM Standard Methods (5) for the chemical determination of ash, extractives, lignin, and carbohydrates were performed on all species to provide the "true" chemical composition or calibration standards.

DISCUSSION

Chemical variations between hard- and softwoods can easily be determined by their respective infrared spectra. For example, Figure 1 illustrates some differences between the FTIR-PAS spectra of a hardwood (acacia) and a softwood (white fir). Hardwoods typically have a higher content of xylan as evidenced by the more intense absorption band at 1730 cm^{-1} (band 1) in Figure 1. Hardwoods also show an absorption at 830 cm^{-1} (band 5) due to syringyl structures characteristic of hardwood lignin. In contrast, softwoods show enhanced absorptions at 870 cm^{-1} and 810 cm^{-1} (bands 3 and 4, respectively) characteristic of the benzene ring substitution of the guaiacyl moieties, the main structural unit of softwood lignins.

The PAS spectra from the different wood species were

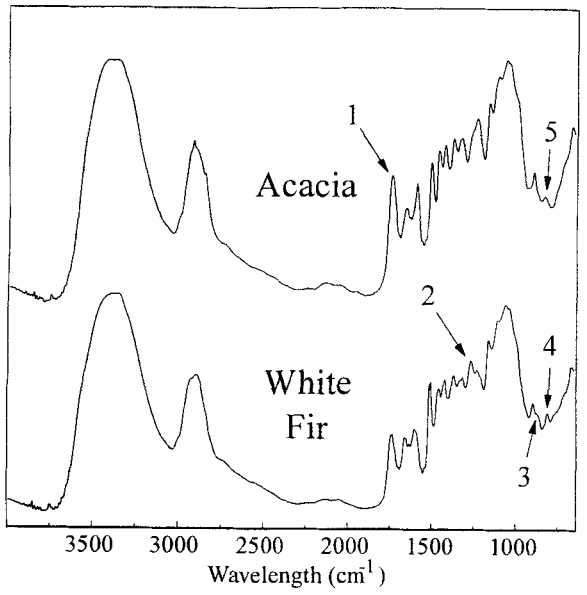

FIGURE 1. FTIR-PAS spectra of hard (acacia) and softwood (white fir). The labeled absorption bands correspond to: 1) C=O stretch in xylan; 2) guaiacyl nuclei in lignin; 3) 1,3,4-substituted benzene ring in softwood lignin; 4) 1,3,4-substituted benzene ring in softwood lignin; and 5) 1,3,4,5-substituted benzene ring in hardwood lignin.

subjected to principal component analysis to determine whether the wood species could be distinguished. The spectral range used for analysis in this study was 1800 to 800 cm^{-1}.

Figure 2 shows the two-vector principal component 1 vs principal component 2 score plot from the principal component analysis of the PAS data. This plot (or species map) shows the overall variation for the PAS spectra. The

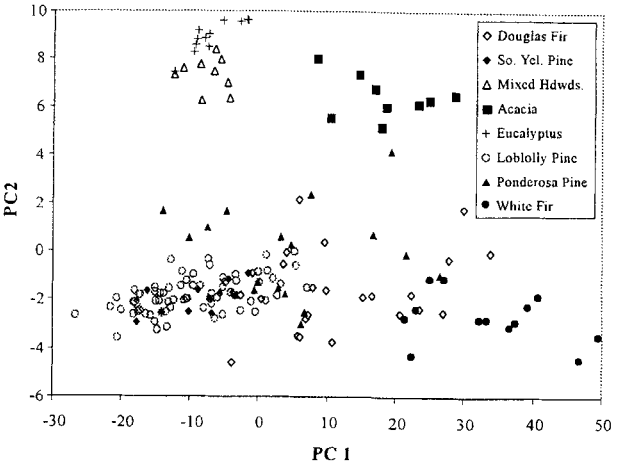

FIGURE 2. Species identification by principle component analysis applied to photoacoustic measurements of milled wood.

different wood species clearly cluster in different spectral space regions, reflecting their chemical similarities. This is demonstrated by noting that all of the hardwoods are located in the upper half of the species map and all softwoods in the lower portion. (While some of the species appear to be overlapped, additional orthogonal projections not shown are required to demonstrate the uniqueness of each species.) The species map also shows that the softwood and hardwood samples further cluster by species type. Note that the loblolly and Southern yellow pines samples occupy the same spectral space as expected, since loblolly pine is a major component of the Southern yellow pines mixture. The first principal factor of the score plot, which accounts for approximately **92%** of the variance in the PAS measurements, contains information about the chemical makeup of the wood samples. The ordinate shows that the second factor, which explains approximately **6%** of the remaining variance, quite clearly separates hard and soft woods.

The range of calibration was augmented by preparing "special" calibration samples. These samples were prepared by manually sorting wood chips into groups which contained primarily heartwood or sapwood, and samples with increased bark and no bark at all. These samples represented the extremes for each species and helped to delineate the species boundaries in qualitative analysis. The species maps confirm that the "extreme" samples span a broader range in spectral space than the unsorted, natural abundance species, as expected and actually formed the boundaries for the respective species.

An important aspect of this work was to demonstrate that quantitative chemical information can be extracted from the PAS infrared measurements. Chemical determination of extractives, lignin, and carbohydrates were performed on all samples using ASTM methods.(5) A full cross-validation PLS calibration model for all three chemical constituents was then developed using three softwood species (douglas fir, white fir and ponderosa pine).

Correlations between the true chemical compositions of the three softwoods and those predicted from the cross-validated PLS regression on PAS measurements for lignin, carbohydrate and extractives content were then made. In all cases, predictions were within the precisions (1%) of the wet chemical methods used to develop the model. Correlation coefficients ranged between 0.85 and 0.94.

While PAS has been demonstrated to provide a laboratory-based rapid alternative to wet chemical analysis, TIRS is capable of providing the same information in near real-time and *on line*. TIRS captures the "fingerprint region" mid-infrared spectra of solid materials moving along a process line. We have applied TIRS to the analysis of wood

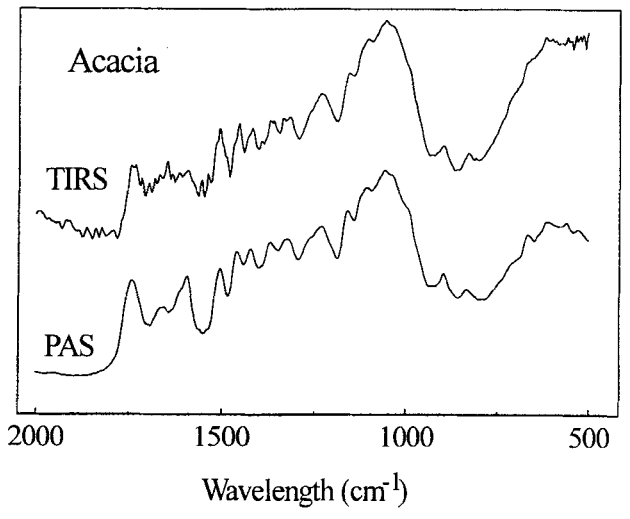

FIGURE 3. Comparison of normalized TIRS and PAS spectra.

chips in laboratory simulations of an on-line environment. As mentioned earlier, TIRS measurements of the moving chips produce similar infrared spectra to that of PAS. Figure 3 shows a comparison of normalized spectra obtained from TIRS and PAS measurements. The spectra are visually similar and PLS calibration modeling confirms that the chemical information content of PAS and TIRS spectra are equivalent. Water vapor bands observed in the TIRS spectrum are present because of the water vapor present in the ambient air between the spectrometer and wood chips. These bands, however, do not interfere with calibration modeling because they are uncorrelated with the chemical compositions of the samples.

TIRS data sets of all eight wood species were collected. A principal component analysis of the TIRS data yielded statistically similar species maps to those produced from PAS spectra. The TIRS principal component species maps also showed clear distinctions of hardwoods and softwoods, and that each wood species occupied a unique region of spectral space.

In order to determine if quantitative chemical information could be obtained from TIRS measurements on moving

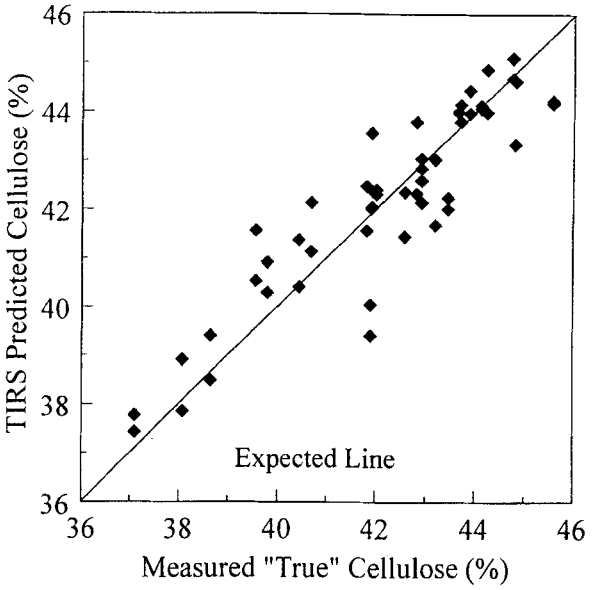

FIGURE 4. Correlation plot for the determination of cellulose based on a simulated on-line TIRS measurement of Douglas fir, ponderosa pine and white fir. RMS error = 0.90.

chips, PLS regression with full cross-validation was performed on the same three softwood species used in the PAS analysis.

As with PAS measurements, good correlations for predictions of lignin, carbohydrate and extractives content were also obtained from TIRS measurements. Figure 4 shows a typical analysis result from a simulated on-line TIRS measurement of wood chips moving at 350 ft/min. Each point in the plot represents a prediction from a model in which it was not a participant, namely full cross-validation modeling was used.

CONCLUSION

These data demonstrate that good quality mid- infrared spectra can rapidly be obtained by both PAS in the laboratory on milled wood and by TIRS on moving wood chips in a simulated on-line system. Chemometric methods such as principal component analysis and PLS modeling have

demonstrated qualitative analysis of wood species. These infrared techniques can rapidly distinguish wood species at- and on-line. In addition, these rapid techniques are capable of quantitative analysis of extractives, lignin, and carbohydrates with accuracies comparable to wet chemical methods. The rapidity and low cost of these methods makes them suitable for use on-line in the paper and pulp industry.

ACKNOWLEDGMENTS

Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under contract No. W-7405-ENG-82. This work is supported by the U. S. Department of Energy, Office of Industrial Technology and is part of the Forest Products Agenda 2020 Initiative .

REFERENCES

1. Meder, R., Gallagher, S., Mackie, K., Bohler, H., and Meglen, R., *Holzforschung*, 1997 (submitted and accepted).
2. Meglen, Robert R., *J. of Chemometrics,* **5**, 163-179, (1991).
3. Kuo M.-L., McClelland, J. F., Chien, P.-L., Walker, R. D., and Hse, C.-Y., *Wood and Fiber Science*, **20**(1), 132-145 (1988).
4. Jones, R. W, and McClelland, J. F., *Process Control and Quality*, **4**, 253-260 (1993).
5. ASTM Standard Methods: E1757-95 wood preparation, E1755-95 ash content, E1756-95 total solids, E1690-95 ethanol extraction, E1721-95 acid insoluble residue, E1758-95 carbohydrates, and TAPPI UM250 acid soluble lignin.